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## 6. AUTHOR(S)

Nicholas J. Turro

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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Box 20, Low Memorial Library  
New York, NY 10027

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## 13. ABSTRACT (Maximum 200 words)

The objectives of the research supported by this AFOSR grant were to create new knowledge concerning the nature and behavior of high energy content materials adsorbed at the liquid liquid, liquid-solid, and the solid gas interfaces. The strategy employed was to use photochemical reactions and photophysical parameters as probes to characterize the structure and dynamics of high energy species. The reactions of radical pairs produced by photochemical excitation of ketones and the electron transfer process between a metal complex and an electron acceptor were employed as general photochemical probes of a range of interfacial regions. The techniques used were a battery of time resolved spectroscopic methods including optical absorption, optical emission, nuclear magnetic resonance and electron spin resonance. The objects achieved were the development of a framework which now allows both the chemistry of high energy species adsorbed at interfaces to be controlled and manipulated and the structure and dynamics of the interfacial region to be better understood.

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# DYNAMICS AND STABILIZATION OF MATERIALS POSSESSING HIGH ENERGY CONTENT

Nicholas J. Turro  
Columbia University  
1991

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## COMPLETED PROJECT SUMMARY

Title: Dynamics and Stabilization of Materials Possessing High Energy Content

Principal Investigator: Dr. Nicholas J. Turro

Inclusive Dates: November 1, 1989 to October 31, 1991

Contract Number: AFOSR-90-0049

Senior Research Personnel: Dr. Naresh D. Ghatila

Junior Research Personnel: Ms. Shufang Niu  
Mr. Chung-Hsi Wu  
Mr. William S. Jenks

### Publications:

1. "Modification of Face Selectivity by Inclusion in Cyclodextrins," W.S. Chung, N.J. Turro, J. Silver and W.J. LeNoble, J. Am. Chem. Soc., 112, 1201 (1990).
2. "Modification of Photochemical Reactivity by Zeolites: Cation Controlled Photodimerization of Acenaphthylene within Faujasites," V. Ramamurthy, D.R. Corbin, C.V. Kumar and N.J. Turro, Tetrahedron Letts., 31, 47 (1990).
3. "Photoinduced Electron-Transfer Reactions to Probe the Structure of Starburst Dendrimers," M.C. Moreno-Bondi, G. Orellana, N.J. Turro and D.A. Tomalia, Macromolecules, 23, 910 (1990).
4. "Combined Effect of Isotopic Substitution, Temperature, and Magnetic Field on the Lifetimes of Triplet Biradicals," J. Phys. Chem., 94, 1144 (1990).
5. "Synthesis of  $^{13}\text{C}$  and  $^2\text{H}$ -Labelled 2-Phenylcyclododecanones," V.P. Rao, J.-F. Wang, N.J. Turro and C.E. Doubleday, Jr., J. Lab. Compds. & Radiopharm, XXVIII, 193 (1990).

6. **"<sup>99</sup>Ru NMR Spectroscopy of Ruthenium(II) Polypyridyl Complexes,"** G. Orellana, A.Kirsch.-De Mesmaeker, and N.J. Turro, *Inorg. Chem.*, **29**, 882 (1990).
7. **"A Fine-Tuning of Photoreactivity of Large Ring 2-Phenylcycloalkanones Adsorbed in Cyclodextrins,"** *Tetrahedron Letts.*, **31**, 835 (1990).
8. **"Physical Organic Photochemistry,"** *J. Photochem. & Photobio., A: Chemistry*, **51**, 63 (1990).
9. **"Laser Flash Photolytic Studies of Arylhalocarbenes,"** R.A. Moss and N.J. Turro, in *"Kinetics and Spectroscopy of Carbenes and Biradicals,"* ed. M.S. Platz, Plenum Publ. Corp., 1990, pp. 213-238.
10. **"Exchange Effects and CIDEP,"** W.S. Jenks and N.J. Turro in *Res. on Chem. Intermediates*, **13**, 237 (1990).
11. **"In Situ Kinetics Measurements of Surfactant Adsorption on Colloidal Alumina using ESR Spectroscopy,"** C.A. Malbrel, P. Somasundaran and N.J. Turro, *J. Coll. & Interf. Sci.*, **137**, 600 (1990).
12. **"Photochemistry of Organic Molecules Adsorbed on Faujasite Zeolites: Steric Effects on Product Distributions,"** N.J. Turro, in *Inclusion Phenomena and Molecular Recognition*, ed. J. Atwood, Plenum Press, 1990, pp. 289-298.
13. **"Photophysical Investigation of Starburst Dendrimers and Their Interactions with Anionic and Cationic Surfactants,"** G. Caminati, N.J. Turro and D.A. Tomalia, *J. Am. Chem.Soc.*, **112**, 8515 (1990).
14. **"Electron Spin Polarization Transfer between Radicals,"** W.S. Jenks and N.J. Turro, *J. Am. Chem. Soc.*, **112**, 9009 (1990).
15. **"Suppression of Chemically Induced Dynamic Nuclear Polarization Enhancements by Nuclei with Large Hyperfine Coupling Constants,"** K.C. Hwang, N.J. Turro, H.D. Roth and C.E. Doubleday, Jr., *J. Phys. Chem.*, **95**, 63 (1991).
16. **"A Comparison between Zeolite-Solvent Slurry and Dry Solid Photolyses,"** V. Ramamurthy, D.R. Corbin, N.J. Turro, Z. Zhang and M. Garcia-Garibay, *J. Org. Chem.*, **56**, 255 (1991).
17. **"Utilization of Radical Scavenging to Develop Nuclear Spin Polarization and Magnetic Isotope Separation in Long Flexible Biradicals,"** N.J. Turro, K.C. Hwang, V.P. Rao and C.E. Doubleday, Jr., *J. Phys. Chem.*, **95**, 1872 (1991).

18. "Octahedral Ru(II) Complexes Containing the Dipyrrophenazine Ring System: Novel Fluorescent Probes for Nucleic Acid Structure," Polym. Preprints, 32, 634 (1991).
19. "Investigation of the Kinetic Window for Generation of  $^{13}\text{C}$  T<sub>0</sub>-S CIDNP Derived from Long-Chain Biradicals by Tuning the Rates of Bimolecular Scavenging and Intersystem Crossing," J. Am. Chem. Soc., 113, 2850 (1991).
20. "Diastereoselective Induction in Radical Coupling Reactions: Photolysis of 2,4-Diphenylpentan-3-ones Adsorbed on Faujasite Zeolites," J. Photochem. Photobiol. A: Chem., 57 7, (1991).
21. "Photoelectron Transfer Between Molecules Adsorbed in Restricted Spaces," in Photochemical Conversion and Storage of Solar Energy, eds. E. Pelizzetti and M. Schiavello, Kluwer Acad. Publ., The Netherlands, 1991, pp. 121-139.
22. "Photochemistry of Large-Ring 2-Phenylcycloalkanones in Various Environments. Intramolecular Para Coupling Products of Acyl Benzyl Biradicals," N. Han, X. Lei and N.J. Turro, J. Org. Chem., 56, 2927 (1991).
23. "Luminescence of Ruthenium(II) Polypyridyls: Evidence for Intercalative Binding to Z-DNA," A.E. Friedman, C.V. Kumar, N.J. Turro and J.K. Barton, Nucl. Acids Res., 19, 2595 (1991).
24. "Diffusion and Percolation of Radical Pairs in Zeolite Media. A Product Analysis Study," J. Am. Chem. Soc., 113, 6212 (1991).
25. "Stereochemistry of Photocycloaddition of (*E*)-1,2-Dicyano- and (*Z*)-1,2-Diethoxyethylene to 5-Substituted Adamantanones," W.-S. Chung, N.J. Turro, S. Srivastava, and W.M. le Noble, J. Org. Chem., 56, 5020 (1991).
26. "Phosphorescence from a Bromonaphthalene Lumophore as a Photophysical Probe of Polymer Conformation and Interpolymer Interactions," Macromol. 24, 4054 (1991).
27. "Interaction of Horse Plasma Gelsolin with the Hydrophobic Fluorescent Probe 2-(N-Methylanilino)Naphthalene-6-Sulfonic Acid," Biochem. Internat., 23, 905 (1991).
28. "Thinking Topologically about Photochemistry in Restricted Spaces," N.J. Turro and M. Garcia-Garibay, in Photochemistry in Organized and Constrained Media, ed. V. Ramamurthy, VCH Publ., 1991, pp. 1-38.
29. "Photophysical Investigation of Similarities between Starburst Dendrimers and Anionic Micelles," J. Am. Chem. Soc., 113, 7335 (1991).

30. "Photoinduced Electron Transfer Quenching of Excited Ru(II) Polypyridyls Bound to DNA: The Role of the Nucleic Acid Double Helix," Photochem. & Photobiol., 54, 499 (1991).
31. "Photoproduction of Remarkable Stable Benzylic Radicals in Cyclodextrin Inclusion Complexes," V.P. Rao, M.B. Zimmt and N.J. Turro, J. Photochem. Photobiol. A: Chem., 60, 355 (1991).
32. "Photochemistry of 2,2,12-Trimethylcyclododecanone and 2,2,12,12-Tetramethylcyclododecanone: Product Distribution, Photo-CIDNP and Magnetic Isotope Effect," N. Han, K.C. Hwang, X. Lei and N.J. Turro, J. Photochem. Photobiol. A: Chem., 61, 35 (1991).
33. "Effect of External Pressure on Photoinduced Electron-Transfer Reactions in the Marcus Inverted Region," W.-S. Chung, N.J. Turro, I.R. Gould and S. Farid, J. Phys. Chem., 95, 7752 (1991).

#### Abstract of Objectives and Accomplishments

The objectives of the research supported by this AFOSR grant were to create new knowledge concerning the nature and behavior of high energy content materials adsorbed at the liquid-liquid, liquid-solid, and the solid-gas interfaces. The strategy employed was to use photochemical reactions and photophysical parameters as probes to characterize the structure and dynamics of high energy species. In particular, the reactions of radical pairs produced by photochemical excitation of ketones and the electron transfer process between a metal complex and an electron acceptor were employed as general photochemical probes of a range of interfacial regions. The techniques employed were a battery of time resolved spectroscopic methods including optical absorption, optical emission, nuclear magnetic resonance and electron spin resonance. The objects achieved were the development of a framework which now allows both the chemistry of high energy species adsorbed at interfaces to be controlled and manipulated and the structure and dynamics of the interfacial region to be better understood.

#### Participating Professionals

##### Collaborators:

Prof. William J. le Noble, SUNY Stony Brook, New York  
Dr. V. Ramamurthy, E.I. duPont de Nemours and Co., Wilmington, DE.  
Dr. David R. Corbin, E.I. duPont de Nemours and Co., Wilmington, DE  
Dr. Challa Vijay Kumar, University of Connecticut, Storrs, CT  
Dr. Donald A. Tomalia, Michigan Molecular Institute, Midland, MI  
Dr. Charles E. Doubleday, Jr., Columbia University, New York, NY  
Professor Andree Kirsch-De Mesmaeker, Universite Libre de Bruxelles, Brussels, Belgium  
Professor Robert A. Moss, Rutgers University, New Brunswick, NJ  
Professor P. Somasundaran, Columbia University School of Engineering and Applied Science, New York, NY  
Professor Heinz D. Roth, Rutgers University, New Brunswick, NJ  
Professor Jacqueline K. Barton, Caltech, Pasadena, CA

Professor L.D. Burtonick, University of British Columbia, Vancouver, B.C.  
Dr. Ian R. Gould, Eastman Kodak Research Lab, Rochester, NY  
Dr. Samir Farid, Eastman Kodak Research Lab, Rochester, NY

**Advanced Degrees Awarded:**

**Jinfang Wang**, Ph.D. Columbia University, February, 1990  
Thesis Title: Dynamics of Flexible Triplet Biradicals. The Importance of Spin Dynamics and Chain Dynamics.

**Nianhe Han**, Ph.D. Columbia University, August 1990  
Thesis Title: Highly Selective Photochlorination of Long Chain n-Alkanes and Substituted n-Alkanes Adsorbed on Ion-Exchanged ZSM-5 Zeolites. Photochemistry of  $\alpha$ -Substituted Large Ring Cycloalkanones.

**Wen Sheng Chung**, Ph.D. Columbia University, May 1990  
Thesis Title: Pressure as a Tool in the Study of Photoinduced Electron-Transfer, Energy Transfer and Cycloaddition Reactions. The Influence of Electronic Effects and Inclusion in Cyclodextrins on the Face Selectivities of Photoinduced Oxetane Formation of 5-Substituted Adamantan-2-ones.

**Kuo-Chu Hwang**, Ph.D. Columbia University, April 1990  
Thesis Title: Effect of Nuclei with a Large Hyperfine Coupling Constant (HFC) on the Pattern and Enhancement of CIDNP of Nuclei with Smaller HFC. CIDNP and Magnetic Isotope Effect in Long Flexible Biradicals: Importance of Chemical Dynamics, Spin Dynamics, Chain Dynamics and Electron Exchange Dynamics.

**William S. Jenks**, Ph.D. Columbia University, February 1991  
Thesis Title: Time Resolved EPR and Photophysical Studies of the Interactions of Doublet and Triplet States with Stable Nitroxides.

**Ann Rachel Leheny**, Ph.D. Columbia University, August 1991  
Thesis Title: Dynamics in Restricted Spaces and Disordered Systems: Investigations of Excitation Relaxation and Molecular Diffusion in Silicalite and Silica Gel.

### Coupling Activities

The Principal Investigator met with Dr. Frederick Hedberg at AFOSR offices in Bolling Air Force Base, D.C. in April 1991 to discuss Air Force interests. In August 1991 Dr. Donald Ball and Dr. Frederick Hedberg of AFOSR visited our laboratories and had discussions with the Principal Investigator about his current research activities. The Principal Investigator attended the Air Force Contractors' Meeting in Irvine, CA on October 20-22, 1991 during which time he presented a poster on his work, "Photophysical Investigation of the Comparison between Starburst Dendrimers and Anionic Micelles" and had discussions with Dr. Larry Burggraf of AFOSR.

The Principal Investigator was presented with the Inter-American Photochemistry Award at a meeting in Clearwater Beach, FL, January 1991. He presented lectures on Air Force supported research at the following universities and industrial sites: Ciba-Geigy Company (Ardsley, NY); Mobil Oil Research & Development (Paulsboro, NJ), E.I. duPont Central Research Dept. (Wilmington, DE), E.I. duPont (Towanda, PA), Unilever USA Research (Edgewater, NJ), IBM Almaden Research Labs (San Jose, CA), Hoechst Chemical Company (Frankfurt, Germany), Bowling Green State University (OH), Pennsylvania State University (University Park, PA), SUNY Binghamton, NY, Caltech (Pasadena, CA), Stanford Univ. (CA), Florida State Univ. (Tallahassee, FL), Universitat Mainz (Germany), Universitat Wurzburg (Germany), Michigan State University (East Lansing, MI), Iowa State University (Ames, IA); and at the following scientific meetings: Asilomar Conference on Spectroscopy (Monterey, CA) in February 1991, American Chemical Society's National Meeting (Organic Division) in New York City, August 1991; American Chemical Society's National Meeting (Physical Division) in Washington, D.C. in August 1990, Inter-American Chemical Photochemistry Society, January 1991, Reaction Mechanisms Conference in Boulder, CO in June 1990, International Conference on the Organic Solid State (Vancouver, B.C.) in July 1991, International Conference on Solar Energy (Palermo, Sicily) July 1990, IUPAC meeting on Organic Reactions in Solution (Canterbury, UK) July 1990, Southeast Section Meeting of the ACS in New Orleans, December 1990.